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14. ABSTRACT Polyhedral Oligomeric Silsesquioxanes (POSS) are nanoparticles that are used to enhance the thermal and mechanical properties of many polymeric systems. Starting in 1993 there has been extensive research in understanding how POSS affects these properties.1-6 Certain POSS macromers can be copolymerized with organic monomers to form nanocomposite type materials. A model is emerging for how addition polymerized POSS copolymers can undergo a type of self assembly to form a nanocomposite.6 The R-group on the POSS moiety (see figure 1) plays a critical role in determining the properties of the nanocomposite, as it determines the level of compatibility of the POSS with the comonomer and how strongly the POSS cages associate. A common (but not always observed) phenomenon with POSS in glassy polymers, is that cyclohexylPOSS often increases thermal transitions while isobutylPOSS frequently plasticizes. It is possible that this is due to the length scale of the POSS-cage domains and/or their level of compatibility with the polymer matrix.					
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REACTIVITY RATIOS OF CYCLOHEXYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS)-STYRENE WITH STYRENE MONOMER (PREPRINT)

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Introduction

Polyhedral Oligomeric Silsesquioxanes (POSS) are nanoparticles that are used to enhance the thermal and mechanical properties of many polymeric systems. Starting in 1993 there has been extensive research in understanding how POSS affects these properties.¹⁻⁶ Certain POSS macromers can be copolymerized with organic monomers to form nanocomposite type materials. A model is emerging for how addition polymerized POSS copolymers can undergo a type of self assembly to form a nanocomposite.⁶ The R-group on the POSS moiety (see figure 1) plays a critical role in determining the properties of the nanocomposite, as it determines the level of compatibility of the POSS with the comonomer and how strongly the POSS cages associate. A common (but not always observed) phenomenon with POSS in glassy polymers, is that cyclohexylPOSS often increases thermal transitions while isobutylPOSS frequently plasticizes. It is possible that this is due to the length scale of the POSS-cage domains and/or their level of compatibility with the polymer matrix.

To help define the microstructure of addition copolymers, the POSS macromer and organic monomer reactivity ratios need to be known. When two monomers are copolymerized, their reactivity ratios (r_1 and r_2) dictate the copolymer microstructure. When r_1 and r_2 are both >1 , the product will be a block copolymer. If r_1 and r_2 are very close to 0, the copolymer will be alternating. If r_1 and r_2 are each close to 1, the copolymer will be random.⁷

Previously, we reported the reactivity ratios of styrene and isobutylPOSS-styrene ($r_1 = 0.84$ and $r_2 = 0.38$) to be indicative of random copolymerization.⁸ We now report the reactivity ratio data for a cyclohexylPOSS-styrene copolymerized with styrene. The synthesis route is shown in figure 1.

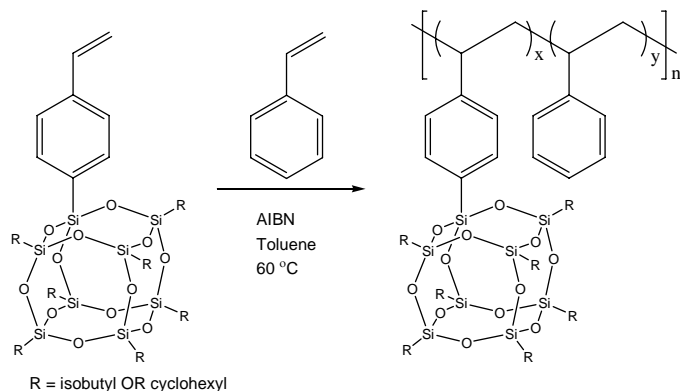


Figure 1. Synthesis of isobutyl or cyclohexylPOSS-PS copolymer.

Experimental

Materials. CyclohexylPOSS-styrene monomer, $(C_6H_{11})_7(Si_8O_{12})(C_8H_7)$, was synthesized according to the literature method.⁹ Styrene was obtained from Aldrich, and was filtered through a column to remove inhibitor, freeze – pump-thawed three times, vacuum transferred to a flask and stored in a freezer under nitrogen prior to use. 2,2'-azobisisobutyronitrile was obtained from Aldrich and was used without further purification. Toluene was passed through an alumina column to remove water, and then freeze-pumped-thawed to remove oxygen. Diethyl ether, chloroform and methanol were obtained from Fisher and were used without further purification.

Instrumentation. ¹H NMR spectra were obtained on a Bruker 400-MHz spectrometer using 5 mm o.d. tubes. Sample concentrations were about 10%

(w/v) in $CDCl_3$ and were referenced internally to residual $CHCl_3$ at 7.26 ppm. Spectra were run with 15 second delays to ensure accurate integrals.

Copolymerizations The copolymerization of POSS-styrene and styrene was initiated by AIBN at 60° C (figure 1). A stock AIBN toluene solution was prepared by adding AIBN (10.40 mg, 0.0633 mmol) in a 100 mL volumetric flask. For the 50 mole % reaction, the POSS-styrene (1.6529 g, 1.500 mmol) was weighed into a 20 mL scintillation vial which contained a stir bar. The vial was then brought into a dry box under nitrogen atmosphere. Styrene (0.159 g, 1.527 mmol) was then added into the vial. The AIBN/toluene solution (6.00 mL) was added to the reaction; the total monomer concentration was 0.50 M, and the AIBN concentration was 0.625 mM. The vial was then sealed and brought out of the dry box. The reaction was placed in an oil bath set at 60° C. After one hour the reaction was removed from the heat to stop the copolymerization before reaching 10% completion. Other reactions followed this same procedure. Methanol (10 mL) was added to the reaction to precipitate out the copolymer. To remove any POSS-styrene monomer from the copolymers, a typical workup procedure is to re-dissolve the precipitate in minimal chloroform or ether and then slowly add methanol until the solution becomes cloudy. Centrifuging the cloudy suspension affords a clear decantate in which the unreacted POSS-styrene is soluble. The copolymers were dried overnight under vacuum at about 45 °C.

Results and Discussion

Copolymer Synthesis and Characterization. To obtain valid reactivity ratio data, it is crucial to perform a series of copolymerizations spanning the full range of mole % POSS-styrene and styrene compositions. It is also necessary to use the same concentrations of monomers and initiator in all cases, and to stop the copolymerizations at low conversion to prevent compositional drift from adversely skewing the results. This was achieved following the procedure detailed in the experimental section. The % POSS in both the feed and as measured in the copolymers is plotted and tabulated below.

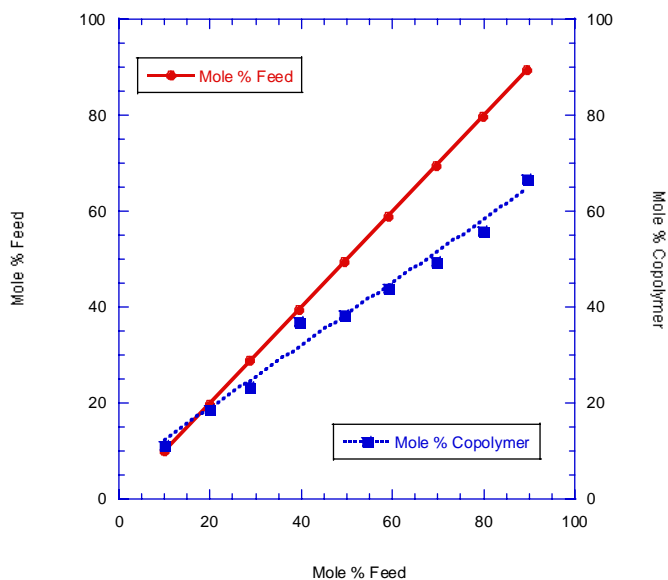


Figure 2. Comparison of the mole % POSS in the feed and the mole % POSS found in the copolymer. The dotted line is what was observed. The solid line is the theoretical composition if both monomers reacted equally.

The mole % POSS data in table 1 is plotted in figure 2. Clearly the % POSS incorporation into the copolymers drops as higher POSS feed levels are used. The relationship is fairly linear, as a least squares fit to the data yields a straight line with a correlation coefficient r^2 of 0.98.

Table 1. The mole % of POSS in the nine reactions ranged from 10 to 90 %.

Experiment #	POSS in Feed		POSS in Copolymer	
	weight %	mole %	weight %	mole %
1	53.92	9.96	56.94	11.10
2	72.34	19.82	70.87	18.70
3	81.05	28.79	76.31	23.34
4	87.32	39.42	86.07	36.87
5	91.22	49.55	86.79	38.34
6	93.83	58.98	89.20	43.83
7	96.02	69.50	91.16	49.37
8	97.65	79.72	93.02	55.73
9	98.91	89.53	95.50	66.71

Characterization The copolymer compositions were determined by analysis of ^1H NMR spectra. To determine the two unknowns, *mole fraction POSS-styrene* (x) and *mole fraction styrene* (y), we need two equations. Equation 1 is simply stating the reasonable assumption that the copolymer composition is based on just these two monomers.

$$x + y = 1 \quad (\text{Eq. 1})$$

The second equation is based on the fact that POSS-styrene and styrene both have different numbers of protons in the aliphatic and aromatic region. We define a term IR (Integral Ratio) as equal to the ratio of the integral value of the aromatic region divided by the integral value of the aliphatic region.

$$IR = \frac{\text{Aromatic Integral}}{\text{Aliphatic Integral}} = \frac{4x + 5y}{80x + 3y} \quad (\text{Eq. 2})$$

In every copolymer, the cyclohexylPOSS-styrene (x component) provides 4 aromatic and 80 aliphatic protons, relative to the styrene (y component) which has 5 aromatic and 3 aliphatic protons. By combining the equations 1 and 2 and solving for mole fraction cyclohexylPOSS-styrene (x) one obtains equation 3.

$$x = \frac{(5 - 3 * IR)}{(77 * IR + 1)} \quad (\text{Eq. 3})$$

For each ^1H NMR spectrum the aromatic integrals and aliphatic integrals were measured and equation 3 was used to determine the % POSS-styrene incorporation. Figure 3 shows a typical ^1H NMR spectrum. The increase in the aromatic integral by the CHCl_3 present in the NMR solvent could be compensated for.

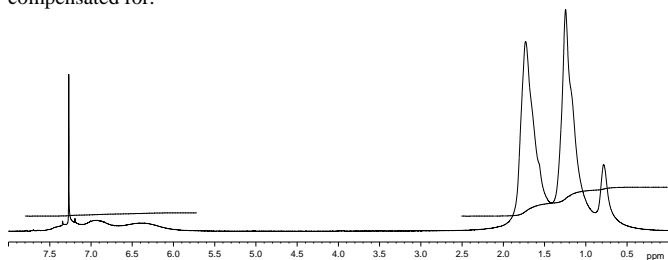


Figure 3 ^1H NMR spectrum of copolymerized CyPOSS-Styrene/Styrene.

Reactivity Ratio Determination. The method used for determining reactivity ratios was the Tidwell & Mortimer non-linear least squares equation.¹⁰ The mole % POSS data in Table 1 yielded results that $r_{\text{styrene}} = 0.80$ and $r_{\text{CyPOSS-styrene}} = 0.14$. The 95 % confidence interval is plotted in figure 4. Previously we found that the reactivity ratios for isobutylPOSS-styrene with styrene were $r_{\text{styrene}} = 0.84$ and $r_{\text{iBuPOSS-styrene}} = 0.38$. Clearly a growing polymer chain terminated with a styrene radical reacts equally well with either isobutyl or cyclohexylPOSS-styrene. The major difference is that the

cyclohexylPOSS-styrene is even less likely to form a short POSS block than the isobutylPOSS-styrene.

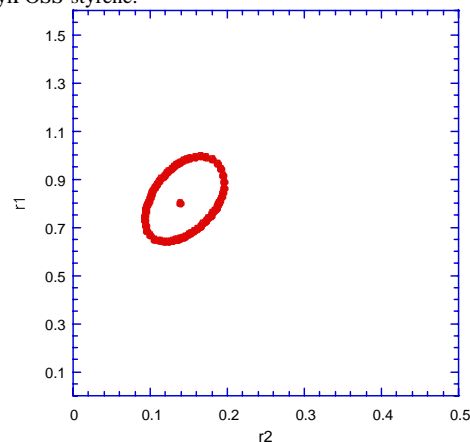


Figure 4. 95 % Confidence Interval from the linear least squares analysis.

Conclusions

Copolymers of styrene and POSS-styrene were synthesized and the reactivity ratio for the two monomers was calculated. POSS-styrene was shown to be reactive when copolymerized with styrene with reactivity ratios of $r_{\text{styrene}} = 0.80$ and $r_{\text{POSS-styrene}} = 0.14$. Therefore, one expects a free radical polymerization to yield fairly random copolymers. A growing polymer chain with a styrene radical on its terminus slightly favors reaction with styrene over a POSS-styrene by a factor of 1.3 ($1/0.80$). A growing polymer chain with a POSS-styrene radical on its terminus much prefers reaction with styrene over POSS-styrene by a factor of 7 ($1/0.14$). For a polymerization taken to completion, compositional drift will certainly result in polymers produced late in the reaction having a higher POSS component than polymers initially formed. However, because POSS is typically used in low mole %'s (10 mole % is around 50 weight %) it is highly unlikely that free radical polymerization will ever generate blocky copolymers. The consequences of this observation are that the POSS aggregation phenomena observed for many different copolymers is a self assembly process and not simply caused by block copolymerization.

Acknowledgments

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